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Properties of the Liquid Crystals Formed by Certain 4′-n-Alkoxyphenyl Biphenyl -4-Carboxylates

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Properties of the Liquid Crystals Formed by Certain 4″-*n*-Alkoxyphenyl Biphenyl-4-Carboxylates

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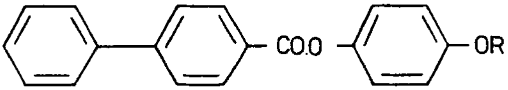
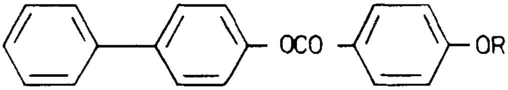
Twelve 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates have been prepared and their liquid crystal transition temperatures determined. Members of the homologous series were studied by differential thermal analysis and the enthalpies of fusion of the various transitions were measured. In contrast with the isomeric homologous series, the 4-biphenylyl 4″-*n*-alkoxybenzoates (previously reported), the 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates do not have smectic mesophases and, in general, have lower liquid crystal transition temperatures and enthalpies of fusion. An explanation for this behaviour is offered.

INTRODUCTION

We have obtained information on the properties (mesophase types, transition temperatures and other thermodynamic data) of the liquid crystals formed by certain members of the homologous series of 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates [(I), where R = *n*-alkyl].



(I)



(II)

A comparison of the properties of these biphenyl-4-carboxylates with those of the isomeric benzoates, the 4-biphenylyl 4″-*n*-alkoxybenzoates (II), which we recently reinvestigated,[1] shows some contrasting features despite the fact that the isomeric homologous series differ only in the manner in which the ester function links the biphenyl and 4-*n*-alkoxyphenyl units of the molecules.

RESULTS AND DISCUSSION

We prepared twelve members (methoxy to *n*-octyloxy and *n*-decyloxy, -dodecyloxy, -tetradecyloxy, and -hexadecyloxy) of the homologous series of 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates. The liquid crystal transition temperatures were measured using a hot stage in conjunction with a polarising microscope, and the existence of all the transitions was confirmed by differential thermal analysis (DTA). The enthalpies of fusion at the various transitions were also determined by DTA. Our results are listed† in Table I, which also gives, in the column headed 'ΔT nematic,' the amount by which the N-I value for a member of the series of benzoates exceeds the value for the corresponding member of the biphenyl-4-carboxylates.

The transition temperatures of the 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates are shown plotted† against the number of atoms, *n*, in the *n*-alkyl chain in Figure 1. The plot shows the usual odd-even alternation of the N-I transition temperatures: two falling curves may be drawn through the points, the lower curve for esters with an odd value of *n*, and the curves converge as *n* increases.

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† The N-I transition temperature for the *n*-propyloxy compound quoted in Table I and plotted in Figure 1 is an estimated value. This compound was troublesome to purify. When subjected to the same purification techniques as the other esters the following transition temperatures were obtained for the *n*-propyloxy compound: C-I, 142°; N-I [132°]. On cooling the isotropic liquid the sample crystallised almost immediately after the appearance of the nematic mesophase. The N-I value of 132° lies somewhat below the value expected for the *n*-propyloxy compound on the assumption that, as *n* increases, the transition temperatures of the odd members of the homologous series lie on a smoothly falling curve. Nevertheless, the N-I value of 132° could not be raised by repeated recrystallisation of the sample, and essentially the same result was found when the *n*-propyloxy compound was synthesised from starting materials obtained from a different source. However, roughly 5% of an impurity was revealed by analytical HPLC as an unresolved shoulder on the ester peak. The material corresponding with the central portion of the ester peak was separated on a semi-preparative HPLC column and was shown to be free of the contaminant by analytical HPLC. As there were no detectable differences in the mass spectrum of the *n*-propyloxy compound recorded before and after purification of the sample the impurity was not identified.

The purified ester still had the C-I transition at 142° but the sample crystallised more readily (at 138°) on slowly cooling the isotropic liquid. Very rapid cooling was required in order to observe the nematic phase at all, and although it was not possible to determine the transition temperature accurately, a reasonable estimate of the value of the monotropic transition temperature for the *n*-propyloxy compound is 136–137°.

TABLE I

Transition temperatures and enthalpies of fusion for 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates (I)

Substituent R	Transition temperatures[a]			ΔT nematic[b]	Enthalpy of fusion[c] ΔH (kcal mol^{-1})
	C-I	C-N	N-I		
CH_3	161°		[140.5°]	7.5°	8.4
C_2H_5	149.5		149.5	7.5	8.2
n-C_3H_7	142		[136–137][d]	2.0–3.0	—
n-C_4H_9		140°	141	2.0	8.4
n-C_5H_{11}		132	132.5	1.0	8.8
n-C_6H_{13}		125.5	134	2.5	8.4
n-C_7H_{15}		111	129	0.5	8.5
n-C_8H_{17}		114	128.5	2.0	9.0
n-$C_{10}H_{21}$		110.5	123.5	3.5	9.3
n-$C_{12}H_{25}$		111.5	119	4.0	12.4
n-$C_{14}H_{29}$		114	116	5.5	9.9
n-$C_{16}H_{33}$		114.5	[113][e]		15.8

[a] Transition temperatures were measured using a Reichert–Kofler hot stage in conjunction with a polarising microscope. The hot stage was calibrated using Analar standards and the precision of measurements thereon is estimated as better than ±0.5°.

[b] ΔT nematic is the difference between the N-I transition temperatures of corresponding 4-biphenylyl 4″-*n*-alkoxybenzoates[1] and 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates.

[c] Enthalpies of fusion were measured using Stanton-Redcroft differential thermal analysers, model 670 and 671, with pure indium wire as the standard. The estimated accuracy of the quoted values is 5%. The ΔH values for the N-I transitions were in the range 0.3–0.18 kcal mol^{-1}.

[d] This is an estimated value—see footnote † of the "Results and Discussion" Section of the text.

[e] The monotropic S_A-N transition for this compound is estimated as 104°. This value was obtained by extrapolation of the monotropic S_A-N values observed for mixtures of the compound with 4-biphenylyl 4″-*n*-tetradecyloxybenzoate.[1] For the following percentages by weight of the 4″-*n*-hexadecyloxyphenyl biphenyl-4-carboxylate in the mixtures, the S_A-N values were: 40%, [114°]; 70%, [110°]; 75%, [109°]; 80%, [108°]; 85%, [107.5°]. When more than 85% of the *n*-hexadecyloxy compound was present the mixtures crystallised before the appearance of the smectic A phase.

[ ] monotropic transition.

As expected, the mode in which the ester group is linked to the rest of the molecule does not markedly influence either the melting points (i.e. the C-I, C-N, or C-S transition temperatures), the N-I transition temperatures, or the transition enthalpies when the two homologous series are considered as a whole. In general, the biphenyl-4-carboxylates have slightly lower numerical values for these physical properties than the analogous benzoates, although for certain isomeric members of the two series some wider differences are apparent.

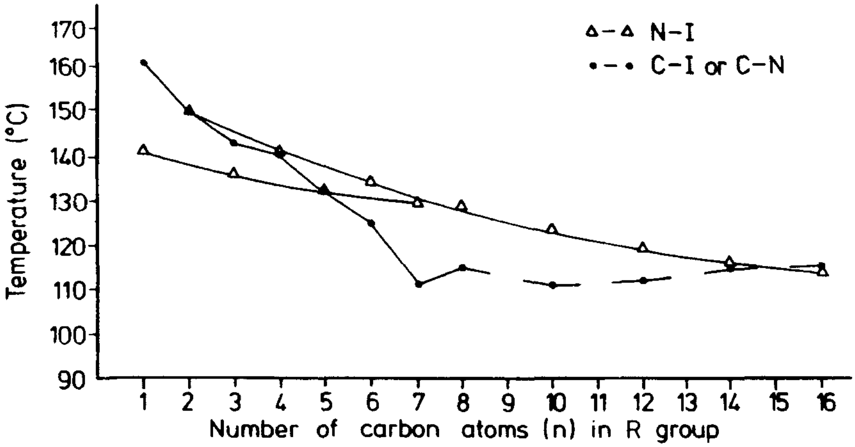

FIGURE 1 Plot of transition temperatures against alkyl chain length (n) for 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates(I).

The average m.p.† of the series of biphenyl-4-carboxylates is 128°. This is roughly 6° lower than the average m.p. of the corresponding benzoates, principally due to the generally higher m.p.s of the earlier members of the series of benzoates which, in contrast to the behaviour of the analogous biphenyl-4-carboxylates, show an odd-even alternation of m.p.

The enthalpies of fusion and the enthalpies of the N-I transitions of corresponding members of the two homologous series are each of the same order of magnitude. However, the average value† of the enthalpy of fusion of the members of the biphenyl-4-carboxylates is 9.13 kcal mol^{-1} and this is lower by more than 1.6 units than the average value of the enthalpy of fusion of the series of benzoates. As was noted with the series of benzoates,[1] as *n* increases the enthalpies of fusion show an odd-even alternation in the opposite sense to that observed for the N-I transition temperatures.

The average value† of the N-I transition temperatures of the biphenyl-4-carboxylates is 3.5° less than that for the corresponding benzoates, but this does not represent a constant difference between the N-I transition temperatures of the two series. The gradients of the curves of the N-I transition temperatures plotted against *n* are different. This can be seen by examination of Table I, which lists, as ΔT nematic, the difference in the N-I transition temperatures of the corresponding benzoates and biphenyl-4-carboxylates. ΔT is initially quite large for both the odd and even members of the two series, but as *n* increases ΔT falls quite rapidly to a value of 0.5° at the *n*-heptyloxy compound. Thereafter, ΔT begins to increase again.

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† Excluding the value for 4″-*n*-hexadecyloxyphenyl biphenyl-4-carboxylate, because data for the corresponding benzoate are not available.

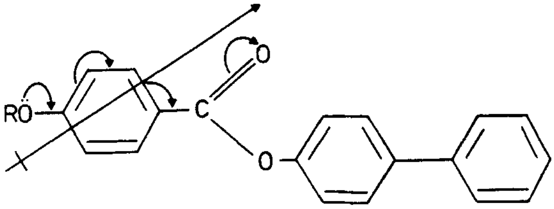
The surprising feature to emerge from a comparison of the properties of the biphenyl-4-carboxylates and the benzoates is that the former series does not show smectic properties. For the benzoates, S_A-N transitions are observed for the *n*-octyloxy, -decyloxy, -dodecyloxy, and -tetradecyloxy compounds. Indeed, when the *n*-tetradecyloxy compound is reached in the series of benzoates, the rising S_A-N and the falling N-I transition temperature curves are only 5° apart.

The biphenyl-4-carboxylates do not show quite the same susceptibility to supercooling of their melts before crystallisation occurs as do the benzoates. For example, the *n*-octyloxy, -decyloxy, -dodecyloxy, and -tetradecyloxy compounds of the series of benzoates could be supercooled to 100°, 98°, 90°, and 92°, respectively, whereas the corresponding biphenyl-4-carboxylates could only be supercooled, respectively to 106°, 100°, 101°, and 106°.

n-Hexadecyloxyphenyl biphenyl-4-carboxylate was prepared, but this ester, the melt of which could be supercooled to 107°, showed only a monotropic N-I transition, confirming that the biphenyl-4-carboxylates are much less prone to form smectic mesophases than the benzoates.

The mesophases formed by mixtures of 4″-*n*-hexadecyloxyphenyl biphenyl-4-carboxylate and 4-biphenylyl 4″-*n*-tetradecyloxybenzoate were studied. The mixtures formed smectic A mesophases up to a composition (by weight) of 85% of the former compound. However, on cooling the mixtures containing more than 85% of 4″-*n*-hexadecyloxyphenyl biphenyl-4-carboxylate solidification of the nematic phase occurred before the N-S_A transition could be detected. Nevertheless, by extrapolation of the S_A-N curve for the mixtures it is estimated that the pure *n*-hexadecyloxy compound would give rise to an S_A-N transition at approximately 104°. Thus, judged by this extrapolated value for the *n*-hexadecyloxy compound the smectic thermal stability of the biphenyl-4-carboxylates is roughly 15° lower than that of the corresponding benzoates.

A possible cause of the different smectic behaviour of the two homologous series of esters may be that conjugation between the alkoxy group and the carbonyl group of the ester function results in a stronger dipole acting across the long molecular axis of the 4-biphenylyl 4″-*n*-alkoxybenzoates than is present in the isomeric 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates. Such a



(III)

dipole (III) is likely to increase the lateral intermolecular cohesive forces and hence the tendency to form smectic mesophases of the former series of esters.

Apart from having an effect on smectic thermal stability, the absence of the dipole (III), resulting in lower intermolecular cohesive forces, may be a contributing factor responsible for the generally lower N-I transition temperatures and enthalpies of fusion of the 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates compared with the corresponding values for the 4-biphenyl 4″-*n*-alkoxybenzoates.

EXPERIMENTAL

4-*n*-Alkoxyphenols

These were prepared by the alkylation of quinol.

Quinol (20 g, 0.182 mol), methylated spirit (30 ml) and the appropriate *n*-alkyl bromide (0.180 mol) were heated gently under reflux. Stirring throughout, a solution of potassium hydroxide (10.7 g) in water (30 ml) was then added, dropwise, during 1 h. After completion of the addition the solution was stirred and heated under reflux for a further 3 h.

The reaction mixture contained unchanged quinol and the required mono-ether (as their sodium salts), and a substantial quantity of the corresponding di-ether. More than one work-up procedure† was tried, but the most efficient was considered to be as follows.

The reaction mixture was cooled, acidified with 6M-aqueous hydrochloric acid, diluted to a volume of 200 ml with water, and extracted several times with hot light petroleum (b.p. 60–80°). The dried extract was concentrated and set aside, when the crude mono-ether (contaminated with the corresponding di-ether) crystallised out. The crude product was purified by column chromatography on silica-gel, eluting with chloroform. The di-ether was present in the first few fractions only. Subsequent fractions, containing the mono-ether, were combined; the chloroform was removed and the pure 4-*n*-alkoxyphenol was obtained by crystallisation from light petroleum (b.p. 60–80°). The yields and m.p.s of the 4-*n*-alkoxyphenols prepared by this method are listed in Table II. Elemental analyses for new 4-*n*-alkoxyphenols are also given in Table II. The 4-methoxyphenol was a recrystallised commercial sample, m.p. 53–55°.

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† The work-up was monitored by thin-layer chromatography (using silica-gel coated plates and chloroform as the solvent). Even substantial amounts of the di-ether could not be detected when the tlc plates were developed with iodine vapour or ultraviolet light. It was necessary to develop the tlc plates by spraying with Millon's reagent[2] followed by heating at 105° for 5 min. The presence of the di-ether was then shown by the appearance of a yellow spot.

TABLE II

4-*n*-Alkoxyphenols prepared by alkylation of quinol

Substituent R	Yield (g)	m.p. (lit. m.p.[a])	Found C	(%) H	Molecular formula	Required C	(%) H
C_2H_5	4.8	66° (65–66°)					
n-C_3H_7	4.2	56 (56–57)					
n-C_4H_9	6.7	64–65 (64–65)					
n-C_5H_{11}	5.9	48–49 (49–50)					
n-C_6H_{13}	8.0	47 (48)					
n-C_7H_{15}	7.8	60–61 (60)					
n-C_8H_{17}	7.2	61 (60–61)					
n-$C_{10}H_{21}$	6.2	71.5	77.0	10.3	$C_{16}H_{26}O_2$	76.8	10.4
n-$C_{12}H_{25}$	6.2	79–80	77.9	10.7	$C_{18}H_{30}O_2$	77.7	10.8
n-$C_{14}H_{29}$	6.1	84–85	78.3	11.2	$C_{20}H_{34}O_2$	78.4	11.1
n-$C_{16}H_{33}$	6.1	88–89	78.9	11.4	$C_{22}H_{38}O_2$	79.1	11.4

[a] Literature m.p.s are those reported by Klarmann, Gatyas, and Shternov.[3]

4″-*n*-Alkoxyphenyl biphenyl-4-carboxylates

These esters were prepared from biphenyl-4-carboxylic acid and the appropriate 4-*n*-alkoxyphenol by the methods described in our previous paper.[1]

As stated in the footnote † of the "Results and Discussion" section, the 4″-*n*-propyloxyphenyl biphenyl-4-carboxylate required purification by HPLC.

Analytical HPLC was carried out with a 15 cm column of Hypersil silica (pore size, 5 μm) eluting with a mixture of heptane, methylene chloride, and isopropyl alcohol (relative ratios by volume, 98.9 : 1.0 : 0.1) at a flow rate of 1 ml/min. Injection onto the column of 20 μl of a solution of the *n*-propyloxy compound (1 mg) in the above solvent (1 ml) gave rise to a single peak (retention time 10.2 min) with a shoulder on the trailing edge (retention time 11.0 min). The area of the shoulder was roughly 5–8% of the area of the main peak. Semi-preparative HPLC was carried out with a Whatman Magnum 9 10/50 column using a Pye LC3 pump, and eluting with a mixture of heptane, methylene chloride, and isopropyl alcohol (relative ratios by volume, 94.9 : 5.0 : 0.1) at a flow rate of 2.7 ml/min. The *n*-propyloxy compound was detected by its ultraviolet absorption at 254 nm. Only the material corresponding with the central portion of the peak was collected. Analytical HPLC showed this to be a single substance.

The purified *n*-propyloxy compound was recrystallised three times from acetone before the determination of its transition temperatures.

The transition temperatures of the 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates are reported in Table I and their elemental analyses are listed in Table III.

TABLE III

Elemental analyses for 4″-*n*-alkoxyphenyl biphenyl-4-carboxylates

Substituent R	Found % C	Found % H	Molecular formula	Required % C	Required % H
CH_3	79.2	5.5	$C_{20}H_{16}O_3$	79.0	5.3
C_2H_5	79.0	5.5	$C_{21}H_{18}O_3$	79.2	5.7
n-C_3H_7	79.4	6.1	$C_{22}H_{20}O_3$	79.5	6.0
n-C_4H_9	79.7	6.6	$C_{23}H_{22}O_3$	79.8	6.4
n-C_5H_{11}	80.2	6.9	$C_{24}H_{24}O_3$	80.0	6.8
n-C_6H_{13}	80.0	7.1	$C_{25}H_{26}O_3$	80.2	7.0
n-C_7H_{15}	80.3	7.3	$C_{26}H_{28}O_3$	80.4	7.2
n-C_8H_{17}	80.5	7.4	$C_{27}H_{30}O_3$	80.6	7.5
n-$C_{10}H_{21}$	81.1	7.9	$C_{29}H_{34}O_3$	80.9	7.9
n-$C_{12}H_{25}$	81.4	8.1	$C_{31}H_{38}O_3$	81.2	8.3
n-$C_{14}H_{29}$	81.6	8.7	$C_{33}H_{42}O_3$	81.5	8.6
n-$C_{16}H_{33}$	81.9	9.1	$C_{35}H_{46}O_3$	81.7	9.0

The following data for 4″-*n*-tetradecyloxyphenyl and 4″-*n*-propyloxyphenyl biphenyl-4-carboxylate are representative of the homologous series as a whole.

n-tetradecyloxy compound: ν_{max} (KBr) 1730, 1610, 1580, 1505, 760 cm^{-1}; δ 0.84–0.92 (br, 3H, CH_3), 1.2–1.9 (br 24H), 4.00 (t, J6.0 Hz, 2H, OCH_2), 6.86 (d, J6.0 Hz, 2H), 7.27 (m, 9H), 8.21 (d, J9.0 Hz, 2H).

n-propyloxy compound: m/e 332 (M^+, 4%), 181 (acylium ion, 100), 182 (13.5), 153 (14), 152 (24).

Acknowledgements

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Corrigendum

At the end of our previous paper,[1] in the data listed for 4-biphenylyl 4″-*n*-pentyloxybenzoate, the NMR absorption at δ 1.1–2.0 should read 1.1–2.0 (m, 6H).